



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 10/00, C07F 5/02 C08F 4/645	A2	(11) International Publication Number: WO 93/21238 (43) International Publication Date: 28 October 1993 (28.10.93)
(21) International Application Number: PCT/US93/02099 (22) International Filing Date: 8 March 1993 (08.03.93) (30) Priority data: 07/868,041 14 April 1992 (14.04.92) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: SIEDLE, Allen, R. ; LAMANNA, William, M. ; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: PETERS, Carolyn, V. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).	(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>	
(54) Title: TRIS(PENTAFLUOROPHENYL)BORANE COMPLEXES AND CATALYSTS DERIVED THEREFROM (57) Abstract <p>Tris(pentafluorophenyl)borane complexes having the general formula $(C_6F_5)_3B-(YXH)_q$ wherein X is oxygen, or sulfur; q is 1 to 3; Y is a hydrogen atom, R^1-, $(R^2)_3Si$, or $(R^3)_2C=N-$; R^1 is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a fluorine-containing hydrocarbyl group; R^2 is independently a linear or branched alkyl group containing 1 to 25 carbon atoms, or a phenyl group, further R^2 may contain a SiO- group; and R^3 is independently a hydrocarbyl group containing 1 to 25 carbon atoms, R^3 may be a hydrogen atom provided both R^3 groups selected are not hydrogen atoms; and to complexes containing the borane complexes with an organometallic compound, either as a neutral compound or as an acidic salt that are useful as catalysts for polymerization and copolymerization of olefins and to polymeric products prepared using these catalysts.</p>		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TC	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

**TRIS(PENTAFLUOROPHENYL)BORANE COMPLEXES AND
CATALYSTS DERIVED THEREFROM**

Field of the Invention

5 This invention relates to complex compounds of
tris(pentafluorophenyl)borane and to mixtures
containing the borane complexes and an organometallic
complex that are useful as catalysts for
polymerization
10 and copolymerization of olefins and to polymeric
products prepared using these catalysts.

Background of the Invention

 Use of soluble Ziegler-Natta type catalyst
15 systems in the polymerization of olefins, in
particular polymerization of ethylene to polyethylene
is known in the art. In general, traditional Ziegler-
Natta type systems comprise a transition metal halide
activated to form a catalyst species by reaction with
20 a metal alkyl cocatalyst, particularly aluminum alkyl
cocatalysts. However, aluminum alkyl cocatalysts are
often used in large excess, see U.S. Patent No.
4,404,344. This is disadvantageous because the
aluminum compounds must be removed from the resultant
25 polymers. These traditional Ziegler-Natta catalysts
often contain a variety of different active sites,
each of which has its own rate of initiation,
propagation, and termination. As a consequence of
this non-uniformity of active sites, the linear
30 polyethylene has a broad molecular weight
distribution. See for example, *Comprehensive
Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon
Press: Oxford, 1982; Vol. 3, Chapter 22.5, p 475;
*Transition Metals and Organometallics as Catalysts for
35 Olefin Polymerization*; Kaminsky, W. and Sinn, H.,
Eds.; Springer-Verlag: New York, 1988, and *Transition
Metal Catalyzed Polymerizations: Alkenes and Dienes*;

Quirk, R.P., Ed.; Harwood: New York 1983.

Recently, catalysts have been reported that rely on boron rather than on aluminum-containing compounds. Boron-based catalysts, in contrast, to the aluminum-based catalysts are often stoichiometric in boron. That is, they contain one mole of boron-containing component per mole of transition metal. Furthermore, it is usually unnecessary to remove the small amount of boron from the polymer, unlike the aluminum-based catalysts, mentioned above.

Tris(pentafluorophenyl)borane $(C_6F_5)_3B$ forms 1:1 complexes with Lewis bases such as ether, amines, and phosphines. The compound is hygroscopic and, presumably forms a monohydrate but neither the composition, that is stoichiometry of this hydrate nor its properties have been disclosed. No uses for these donor-acceptor complexes have been taught, see Massey et al. *J. Organomet. Chem.* 1964, 2, 245. Hygroscopic $(C_6F_5)_3B-Et_2O$ was reported by Pohlman et al. *Z. Nat.* 1965, 20b, 5.

Hlatky et al. *J. Am. Chem. Soc.* 1989, 111, 2728 described zwitterionic catalysts such as $(Me_5Cp)_2Zr[(m-C_6H_4)BPh_3]$. EPO 0 277 004 describes catalysts prepared by reacting, $(Me_5Cp)_2ZrMe_2$ with $B_9C_2H_{13}$, $[Bu_3NH][(B_9C_2H_{11})_2Co]$ or $[Bu_3NH][B_9C_2H_{12}]$.

Similarly, EPO 0 418044 describes monocyclopentadienyl complex catalysts containing a non-coordinating, compatible anion such as $(C_6F_5)_4B^-$. More recently, homogeneous catalysts exemplified by $[Cp_2ZrMe][MeB(C_6F_5)_3]$ have been synthesized from the reaction of Cp_2ZrMe_2 and $(C_6F_5)_3B$ see X. Yang et al. *J. Am. Chem. Soc.* 1991, 113, 3623.

Furthermore, the above described catalysts are sparingly soluble in toluene. The catalysts are even less soluble in normally liquid α -olefins such as 1-hexene or in mixtures of such olefins and non-reactive solvents, such as hexane, toluene or xylene. These

catalysts generally separate as oils from toluene or toluene-hexane mixtures. Even though catalysis still proceeds, phase separation is undesirable for several reasons, for example contact between soluble. When
5 the catalyst is incompletely soluble, catalyzed polymerization typically takes place at different rates either in solution or at the solid-liquid interface, thus tending to lead to a broad distribution of polymer molecular weights.
10 Furthermore, catalyst:monomer ratio in solution is generally difficult to control when the catalyst is only partially soluble.

It is further known that a soluble or molecularly dispersed catalyst typically permits more ready access
15 of the substrate to the active sites. As a result, more efficient use of the catalyst is possible. It is also recognized that the molecular weight of a polymer is proportional to the concentration of monomer in the reaction mixture in which it is synthesized.
20 Generally, high molecular weight is desirable in applications such as glues and adhesives, as well as in the construction of rigid objects such as gaskets, insulators and packaging materials.

Catalytic polymerization of lower olefins, in
25 particular ethylene and propylene is relatively easy. On the other hand polymerization of longer chain α -olefins tends to be slower and the products are often oligomers rather than high polymers, see Skupinska Chem. Rev. 1991, 91, 635. Heterogeneous catalysts
30 such as $\text{TiCl}_3/\text{AlEt}_3$, which produce higher molecular weight polymers from long-chain α -olefins, lead to a broad range of molecular weights (high polydispersity index).

Summary of the Invention

Briefly, in one aspect of the present invention catalyst precursor complexes are provided comprising tris(pentafluorophenyl)borane, $(C_6F_5)_3B$ and at least one
5 complexing compound such as water, alcohols, mercaptans, silanols, and oximes. These neutral complexes may be converted to acidic salts of their conjugate bases by reaction with amines. The neutral complexes or acidic salts are reacted with Periodic
10 Table Group IVB organometallic compounds to form catalytically active compounds (hereinafter also referred to as catalysts) useful for polymerization of olefin monomers. Advantageously, the catalysts of the present invention are soluble in olefins to the extent
15 of 1×10^{-3} molar (M) or greater. Catalysts that can function in undiluted monomer, as distinguished from monomer dissolved in inert diluent, are desirable because the catalysts and monomers tend to produce products having higher molecular weight.
20 Additionally, because only low levels of the catalysts are used, removal of catalyst or its components from the final, product polymer is generally not required.

Catalysts of the present invention may be used to prepare polyolefins from olefinically unsaturated
25 monomers having 2 to 30, preferably 5 to 10 carbon atoms. The resulting polymers have a weight average molecular weight of 100,000 to 5,000,000, preferably 500,000 to 3,500,000 and have a polydispersity (PD) of molecular weights ≤ 3.5 , preferably 1.5 to 3.
30 Polymers prepared from long chain α -olefins having high molecular weight and low polydispersibility are not previously described.

Suitable olefinically unsaturated monomers that may be polymerized using the catalysts of the present
35 invention include, but are not limited to, linear- and branched α -olefins, cyclic olefins, olefins containing an aromatic group such as phenyl, olefins

containing silicon and boron, and diolefins. Mixtures of these of monomers, as well as mixtures containing olefins and diolefins may be copolymerized. Preferred unsaturated monomers include linear α -olefins having the general formula C_nH_{2n} , where n is 5 to 10.

A feature of the present invention is the incorporation of anions of the type $YX-B(C_6F_5)_3^-$ into novel complex salts of Group IVB transition metals (titanium, zirconium, and hafnium), to produce highly active catalysts capable of polymerizing longer chain poly- α -olefins to yield products having very high molecular weights and a narrow polydispersity index. Furthermore, preparation of these salts are described, and such salts can either contain or are essentially free of Lewis bases. An additional feature of this invention is the incorporation of flat carbocyclic ligands into these novel complex salts, to produce olefin polymers of exceptionally high molecular weight. Thus, as shown below using $[(\text{ligand})_2\text{ZrMe}][(\text{C}_6\text{F}_5)_3\text{BOC}_{18}\text{H}_{37}]$ as the catalyst and 1-hexane as the monomer, polymer molecular weight increases as the ligand is changed in the order of cyclopentadienyl < indenyl << fluorenyl. The fluorenyl ligand is therefore particularly useful when high molecular weight, rubbery polyolefins are desired.

In this application:

"Cp" means a carbocyclic ligand, such as cyclopentadienyl, indenyl or fluorenyl;

"Me" means a methyl group;

"Et" means an ethyl group;

"Bu" means a butyl group;

"Ph" means a phenyl group;

"hydrocarbyl" is used in its usual sense to mean a group containing hydrogen and carbon atoms, such as alkyl, alkenyl, aryl, cycloalkyl, cycloalkenyl,

alkaryl, arylalkyl, and the like; and

"Group IVA" and "Group IVB" are the Periodic Table CAS version designations.

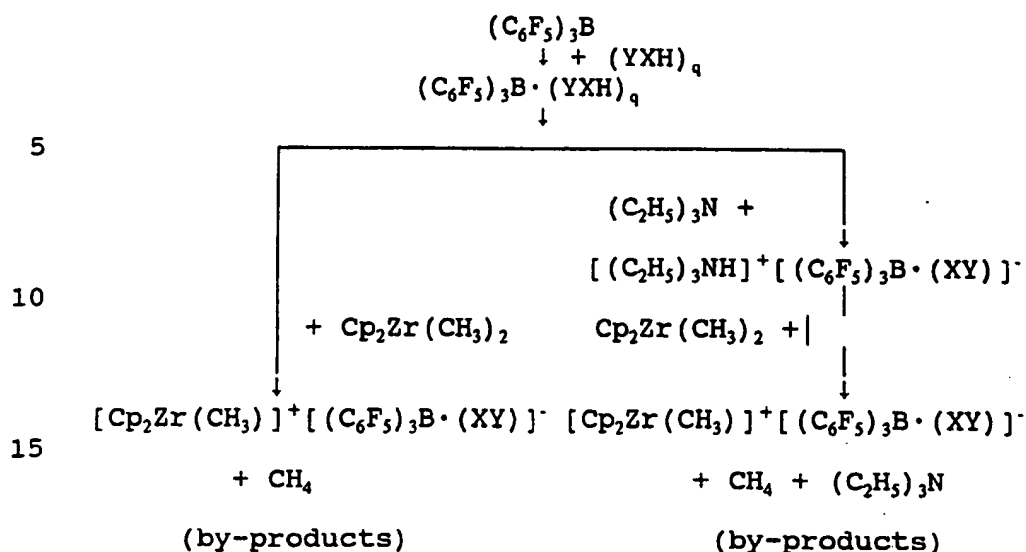
5 Detailed Description of the Preferred Embodiment

The compound $(C_6F_5)_3B$,
tris(pentafluorophenyl)borane (also referred to as
tris(pentafluorophenyl)boron), forms Lewis base
complexes with a wide variety of alcohols, mercaptans,
10 silanols, and oximes. These borane complexes are
catalyst precursors that when combined with Group IVB
organometallic compounds produce catalysts useful for
polymerization of olefins, such that the polymers have
high molecular weights and low polydispersities, that
15 is a narrow molecular weight distribution.

Lewis base complexes of $(C_6F_5)_3B$ bearing at least
one acidic hydrogen atom on the boron-bound heteroatom
are useful for preparing catalysts. These compounds
can be represented by the general formula:
20 $(C_6F_5)_3B \cdot (YXH)_q$ wherein X, Y and q are as described
below and the valence of X is completed with hydrogen
atoms where necessary to provide a neutral compound.

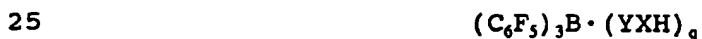
The following reaction scheme illustrates how
neutral Lewis base complexes of
25 tris(pentafluorophenyl)borane and corresponding acidic
salts may be prepared. For illustration purposes, the
reaction scheme depicts $(C_2H_5)_3N$ as a reactant to
produce acidic salts. Without intending to be bound
by theory, reaction scheme further illustrates how the
30 neutral Lewis base complexes of
tris(pentafluorophenyl)borane and the corresponding
acidic salts are believed to react with Group IVB
organometallic complexes to produce the catalytically
active salts of this invention.

7



wherein Y, X, and q are as define below

The neutral borane complexes have the general formula



wherein X is oxygen, or sulfur;

q is 1 to 3, preferably q is 1;

Y is a hydrogen atom, R^1- , $(R^2)_3\text{-Si}$, or $(R^3)_2\text{C=N-}$;

R¹ is a hydrocarbaryl group containing 1 to 500,

30 preferably 1 to 100 carbon atoms, and may contain
a divalent oxygen and further may be a halogen-
containing hydrocarbyl group, for example the R¹
group can be CH₃OC₂H₄-, t-butylcyclohexyl,
isopropyl, allyl, benzyl, methyl, ethyl, C₁₈H₃₇,
35 oligomeric poly-α-olefins (containing 2 to 100
monomeric units), or CF₃CF₂(C₂F₄)_nC₂H₄-, where n has
an average value of 3.5;

R² is independently a linear or branched alkyl group containing 1 to 25 carbon atoms, or a phenyl group, further R² may contain a SiO-group, for example (R²)₃ may be (t-C₄H₉)(CH₃)₂- or ((CH₃)₃SiO)₃-; and

R³ is independently a hydrocarbonyl group containing 1 to

25 carbon atoms, further R^3 may be a hydrogen atom provided both R^3 groups selected are not hydrogen atoms, for example when X is oxygen, $(R^3)_2C=NOH$ forms oximes, a compound (either *cis* or *trans*) containing the oxime group $=C=NOH$, and is a condensation product of aldehydes or ketones with hydroxylamine.

Tris(pentafluorophenyl)borane tends to form complexes with alcohols having the general formula R^1OH . For example, treatment of $(C_6F_5)_3B$ with methanol liquid or vapor produces the bis(solvate) $(C_6F_5)_3B \cdot 2MeOH$. No significant amount of methanol can be removed by pumping at room temperature. This compound can be converted to $(C_6F_5)_3B \cdot MeOH$ by treatment with one equivalent of $(C_6F_5)_3B$. The 1:1 complex $(C_6F_5)_3B \cdot MeOH$ may also be prepared by reacting $(C_6F_5)_3B$ with one equivalent of methanol. Isopropanol forms a bis(solvate) as well but one equivalent of alcohol is removed under vacuum at room temperature.

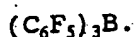
Tris(pentafluorophenyl)boron complexes of less volatile alcohols can be prepared by combining one equivalent each of an alcohol and $(C_6F_5)_3B$ in a suitable, nonreactive solvent such as chloroform or toluene, followed by evaporation of the solvent. Suitable alcohols contain a wide variety of aliphatic or aromatic groups including but not limited to linear (stearyl alcohol), cyclic (t-butylcyclohexanol), branched (isopropanol), unsaturated (allyl alcohol), aromatic (benzyl alcohol), optically active (menthol), oxygen-substituted ($MeOC_2H_4OH$), oligomeric (poly-1-hexene alcohol), and halogen-substituted $[CF_3CF_2(C_2F_4)_n C_2H_4OH]$, where n has an average value of 3.5.

Suitable alcohols generally have pK_a values between -2 and -4. For example, 2,2,2-trifluoroethanol and phenol do not form isorable complexes. Formation of a stable complex is readily ascertained by boron

nuclear magnetic resonance (^{11}B NMR) spectroscopy. The $(\text{C}_6\text{F}_5)_3\text{B}$ complexes of this invention have chemical shifts between -5 and + 15 ppm (relative to external $\text{BF}_3\cdot\text{OEt}_2$) compared with +60 ppm for the swung material $(\text{C}_6\text{F}_5)_3\text{B}$.

5 Other specific examples of $(\text{YXH})_q$ (when q is 1) include silanols $(\text{R}^2)_3\text{SiOH}$, mercaptans (R^1SH) , and oximes $(\text{R}_3\text{C}=\text{NOH})$. Examples of silanols include but are not limited to $(t\text{-C}_4\text{H}_9)_2\text{SiOH}$ and $(\text{Me}_3\text{SiO})_3\text{SiOH}$. Higher mercaptans having low vapor pressures are
10 preferred in catalyst applications such that the polymers produced do not have an objectionable odor. An example of a mercaptan useful in the present invention is octadecyl mercaptan. Examples of oximes include acetone oxime and cyclohexanone oxime.

15 Of the class of compounds of the type $(\text{C}_6\text{F}_5)_3\text{B}-(\text{YXH})_q$, when Y is hydrogen, X is oxygen, and q is 1 or 3, the complex with water is a special case. Exposure of anhydrous $(\text{C}_6\text{F}_5)_3\text{B}$ to water vapor, produces $(\text{C}_6\text{F}_5)_3\text{B}\cdot 3\text{H}_2\text{O}$, a white, stable solid. No intermediate
20 hydrate was detected by infrared spectroscopic analysis. The water content was demonstrated by a single crystal X-ray structure determination. Formation of a trihydrate was unexpected because all other previously known $(\text{C}_6\text{F}_5)_3\text{B}$ complexes with Lewis
25 bases have a 1:1 stoichiometry. Vacuum sublimation of the trihydrate produced a mixture of the monohydrate and $(\text{C}_6\text{F}_5)_3\text{B}$. The pure monohydrate, $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{H}_2\text{O}$, however may be obtained by combining in organic solvents, such as toluene or chloroform, one equivalent of $(\text{C}_6\text{F}_5)_3\text{B}\cdot 3\text{H}_2\text{O}$
30 with two equivalents of $(\text{C}_6\text{F}_5)_3\text{B}$ followed by evaporation of the solvent. This conproportionation reaction is a convenient way of synthesizing the monohydrate as needed. Unlike $(\text{C}_6\text{F}_5)_3\text{B}\cdot 3\text{H}_2\text{O}$, $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{H}_2\text{O}$ is unstable and slowly decomposes, either in solution or in the solid
35 state, to $(\text{C}_6\text{F}_5)_2\text{BOH}$ and $\text{C}_6\text{F}_5\text{H}$. The monohydrate may also be prepared by combining one mole each of water and



The heteroatom-bound protons in Lewis base complexes of $(\text{C}_6\text{F}_5)_3\text{B}$, such as $(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{R}^1\text{OH}$ and $(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{R}^1\text{SH}$ are acidic and can be removed by treatment with bases such as primary, secondary, or tertiary amines. For example, reaction of $(\text{C}_2\text{H}_5)_3\text{N}$ with $(\text{C}_6\text{F}_5)_3\text{B} \cdot 3\text{H}_2\text{O}$ or $(\text{C}_6\text{F}_5)_3\text{B} \cdot 2\text{CH}_3\text{OH}$ produces the acidic salts $[(\text{C}_2\text{H}_5)_3\text{NH}]^+[(\text{C}_6\text{F}_5)_3\text{BOH}]^-$ and $[\text{Et}_3\text{NH}]^+[(\text{C}_6\text{F}_5)_3\text{BOCH}_3]^-$ respectively. Preferred bases are triethylamine, tributylamine and N,N-dimethylaniline.

Catalysts useful for polymerization of olefinic hydrocarbons may be prepared using the precursor borane complexes and hydrocarbylcyclopentadienyl metal complexes having the general formula:



wherein M is titanium, zirconium or hafnium;

p is 1 or 2

Cp is a cyclopentadienyl ligand, wherein each

carbon atom in the ring may be,

independently, substituted with a radical

selected from the group consisting of

hydrocarbyl radicals, hydrocarbyl-substituted

metalloid radicals wherein the metalloid is

selected from Group IVA of the Periodic Table

of the elements wherein the hydrocarbyl and

substituted-hydrocarbyl radicals contain 1 to

20 carbon atoms and can include straight and

branched alkyl groups, cyclic hydrocarbon

groups, alkyl-substituted cyclic hydrocarbon

groups, aromatic groups or alkyl-substituted

aromatic groups; one or two pairs of adjacent

hydrogen atoms of the cyclopentadienyl ligand

may be substituted with one or two $-(\text{CH})_4$

groups to form indenyl or fluorenyl radicals,

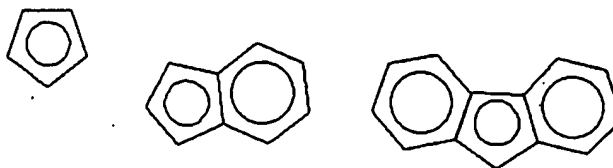
respectively; further, compounds in which one

or two methylene rings having the general

formula $(\text{CH}_2)_n$ wherein n is 3 to 6 may be

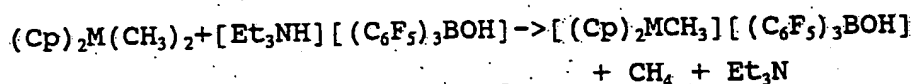
substituted for two adjacent hydrogen groups in the cyclopentadienyl ligand; further, when p is 2, the cyclopentadienyl ligands may be combined into one bidentate ligand molecule by connecting the cyclopentadienyl ligands by an organic or organometalloid group; and R₄ is independently hydrogen or a hydrocarbyl or substituted-hydrocarbyl group containing from 1 to 20 carbon atoms and may be a straight or branched alkyl group, and if sufficiently large enough, a cyclic hydrocarbyl group, an alkyl-substituted cyclohydrocarbyl group, an aromatic group, an aromatics-substituted alkyl group (e.g., benzyl), or an alkyl-substituted aromatic group and also include trisubstituted organometalloid groups of Group IVA elements wherein each hydrocarbyl group on the metalloid contains from 1 to 20 carbon atoms.

Suitable examples of Cp include but are not limited to cyclopentadienyl, indenyl, fluorenyl, bis(octahydrofluorenyl), 1,2-bis(1-indenyl)ethane, 1,2-bis(tetrahydroindenyl)ethane, isopropyl(cyclopentadienyl-1-fluorenyl) and 1,3-bis(9-fluorene)propane. Chiral metallocenes are also suitable and useful when a stereoregular polymer is desired. General structures of cyclopentadienyl, indenyl and fluorenyl ligands, respectively are represented below.



While not intending to be bound by theory, the organometallic complex, $(\text{Cp})_p\text{M}(\text{R}^4)_{4-p}$, is believed to react with acid salts of the anions, such as $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OR}^1$, $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OH}$, $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{SR}^1$, $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OSi}(\text{R}^2)_3$ or $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{ON}=\text{C}(\text{R}^3)_2$ (containing at least one acid proton in the cationic portion of the salt) to form byproducts and catalytically active salts containing $(\text{Cp})_p\text{M}(\text{R}_4)_{3-p}^+$. For example, this can be illustrated by the following reaction with $[\text{EtNH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$.

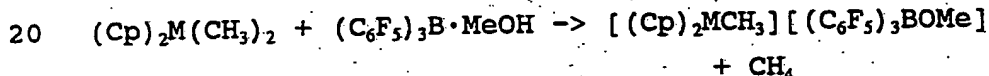
10



(Reaction Scheme I)

15

Alternatively, the need for an acidic salt can be by-passed in the direct reaction of the metal complexes with neutral complexes of tris(pentafluorophenyl)borane with water, alcohols, mercaptans, silanols or oximes. For example,



(Reaction Scheme II)

Materials prepared by either route can be used as catalysts for the polymerization of olefins.

25 Importantly, catalysts prepared according to Reaction Scheme II can be obtained free of extraneous Lewis base byproduct such as triethylamine (obtained in Scheme I).

Materials described in this invention are useful for polymerization of olefins such as ethylene and propylene and in particular higher olefins, for example, 1-hexene or 1-octene. Polyolefins having high weight average molecular weights may be prepared by treating undiluted olefins with a catalytically effective amount of a catalyst of the present invention. Optionally, the polyolefins may be diluted with an inert diluent, such as toluene or hexane.

Catalysts of the present invention may be used to

- prepare polyolefins from olefinically unsaturated monomers having from 2 to 30, preferably 5 to 10 carbon atoms. The resulting polymers have a weight average molecular weight of 100,000 to 5,000,000, preferably
- 5 500,000 to 3,500,000 and have a polydispersity (PD) of molecular weights ≤ 3.5 , preferably 1.5 to 3. Polymers prepared from longer chain olefins, for example, C_nH_{2n} ($n \geq 5$) olefins having high molecular weight and low polydispersity have not been previously described.
- 10 Olefinically unsaturated monomers that may be polymerized using the catalysts of the present invention include, but are not limited to, linear- and branched α -olefins, cyclic olefins, olefins containing an aromatic group such as phenyl, olefins containing
- 15 silicon and boron, and diolefins. Mixtures of these of monomers, as well as mixtures containing olefins and diolefins may be copolymerized.

Table 1

**Polyhexanes Obtained
with
Different Metanocenium Ion Catalysts^(a)**

5

10

15

20

25

Initiator	Degree of Polymerization ^(b)	% Conversion
Cp_2ZrMe^+	99	100
$(\text{indenyl})_2\text{ZrMe}^+$	200	70
$(\text{Me}_5\text{Cp})_2\text{ZrMe}^+$	83	100
$[(\text{Me}_3\text{Si})_2\text{Cp}]_2\text{HfMe}^+$	66	51
$(\text{Me}_5\text{Cp})_2\text{HfMe}^+$	118	100
$(\text{Me}_3\text{SiCp})_2\text{HfMe}^+$	60	98
$(\text{Me}_3\text{SiCp})_2\text{HfMe}^{+ (c)}$	56	90
Cp_2HfMe^+	429	100
$\text{Cp}_2\text{HfMe}^{+ (d)}$	506	100
$(\text{indenyl})_2\text{HfMe}^+$	1025	100
$(\text{Me}_3\text{SiCH}_2\text{Cp})_2\text{ZrMe}^+$	19	4
$(n\text{-C}_8\text{H}_{17}\text{Cp})_2\text{HfMe}^+$	23	94
$(\text{Me}_3\text{SiCp})_2\text{ZrMe}^+$	10	55
$[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{ZrMe}^+$	4	<1
$(\text{PhCH}_2\text{SiMe}_2\text{Cp})_2\text{ZrMe}^+$	7	88
$(\text{fluorenyl})_2\text{ZrMe}^+$	4800	69
$[(\text{indenyl})_2\text{C}_2\text{H}_4]\text{ZrMe}^+$	156	87
$[(\text{indenyl})_2\text{C}_2\text{H}_4]\text{HfMe}^+$	271	78

(a) Conditions: $\text{C}_{18}\text{H}_{37}\text{O} \cdot \text{B}(\text{C}_6\text{F}_5)_3$ salts in 0.5 mL toluene-1-hexene, monomer:catalyst 6400:1 at 0°C

(b) determined by ^1H NMR analysis and refers to the average number of monomer units in the polymer chain

(c) anion is $\text{C}_{18}\text{H}_{37}\text{S} \cdot \text{B}(\text{C}_6\text{F}_5)_3$

(d) anion is conjugate base of polyhexene alcohol $\cdot \text{B}(\text{C}_6\text{F}_5)_3$

35

Ring substitution on the Cp ligand in the catalysts of the present invention can lead to reduced polymer molecular weight and activity. This is illustrated in Table 1. Reduction of polymer molecular weight is generally undesirable in many applications since it is associated with loss of polymer cohesive strength. For example, decreases in molecular weight

40

associated with the Me_3Si group has not been described before. It is surprising because catalysts prepared from $(\text{Me}_3\text{SiCp})_2\text{ZrMe}_2$ and methyl aluminoxane tend to produce higher molecular weight polyhexane than does unsubstituted Cp_2ZrMe_2 .

An advantage of the present invention is the permissible introduction of solubilizing groups that enhance solubility of catalyst salts in the olefinic monomer or solution of monomer and solvent into the anion rather than the cation that contains the active catalytic site. The solubilizing groups are spatially removed from the active site, and therefore do not interfere with polymerization and thus produce polymers of high molecular weight. For example, the catalyst $[(\text{indenyl})_2\text{ZrMe}][(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OC}_{18}\text{H}_{37}]$, in which the anion contains the solubilizing octadecyl group that was introduced via of the alcohol Complex $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{C}_{18}\text{H}_{37}\text{OH}$, is soluble to the extent of about 10^{-3} M in 80:1 (v/v) 1-hexene-toluene. In an other example, polyhexene alcohol having an average degree of polymerization of 5.9 and bearing a terminal CH_2OH group, yielded a solution as concentrated as 10^{-3} M in 40:1 hexene-hexane. For example, the structure of the solubilizing group can be varied so as to produce good catalyst solubility in a monomer of choice by suitably modifying the structure of R^1OH in $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{R}^1\text{OH}$. As illustrated in the examples below, the anions of the present invention provide catalysts that produce higher molecular weight polyolefins than superficially related catalysts, even at equivalent monomer: catalyst ratios.

Although $(\text{indenyl})_2\text{ZrMe}_2$ organometallic compounds are reportedly useful in the preparation of catalysts, there appears to be no correlation between the structure of the ligand(s) in the organometallic portion of the catalyst and the molecular weights of polymers of higher olefins (C5 and greater) produced with such catalysts. As a result, it is not readily

apparent which organometallic compounds may be used to prepare high molecular weight polymers. For example, the soluble, homogeneous olefin polymerization catalysts described by U.S. Patent No. 4,404,344

- 5 (Kaminsky et al.) when used to prepare poly(hexene), produces oligomers having molecular weights less than 50,000.

Structurally, flat cyclopentadienyl ligands, when incorporated into these complex salts, produce polymers
10 of high molecular weight. As shown in Table 1 above, using $[(\text{ligand})_2\text{ZrMe}][(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OC}_{18}\text{H}_{37}]$ as the catalyst and 1-hexene as the monomer, the degree of polymerization in the product polymer increased from 99 to 200 to 4800 as the ligand was changed in the order from
15 cyclopentadienyl to indenyl to fluorenyl, respectively. The fluorenyl ligand is particularly useful when high molecular weight, rubbery polyolefins are desired.

Objects and advantages of this invention are further illustrated by the following examples, but the
20 particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit the invention.

25

Examples

All compounds were characterized by at least one of infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies. NMR analysis included ^1H , ^{11}B , ^{13}C , and ^{19}F . Number average molecular weight (M_n) and weight
30 average molecular weight (M_w) for polymers having M_w less than 10^6 were determined by gel permeation chromatography (GPC) using polystyrene standards or by NMR analysis as is known to those skilled in this art. Polydispersity (PD) refers to the weight-average
35 molecular weight divided by the number average molecular weight, that is, M_w/M_n .

Materials whose weight average molecular weight

exceeded 10^6 were characterized by low angle laser light scattering techniques as is known to those skilled in this art. All starting materials and solvents are commercial available or known in the literature, unless otherwise stated or apparent. All commercially available materials and solvents are available from Aldrich Chemical Co., unless otherwise noted.

Preparation Example 1

10 Preparation of $(C_6F_5)_3B$

Tris(pentafluorophenyl)borane was prepared by the reaction of C_6F_5Li with BCl_3 in hexane at temperatures below $-50^\circ C$ according to the procedure described in Massey et al. *J. Organomet. Chem.* 1964, 2, 245.

15

Example 1

Preparation of $(C_6F_5)_3B \cdot 3H_2O$

A 0.87 gram quantity of $(C_6F_5)_3B$ was placed in one leg of a reactor consisting of an inverted U-tube, closed at both ends and fitted with a stopcock and O-ring joint so that the apparatus could be connected to a vacuum line. Excess water was placed in the other leg. After the water had been frozen with a low temperature bath, the apparatus was evacuated. After warming the reactor to room temperature, the borane reacted with water vapor to form the trihydrate. After water uptake was completed, excess water was pumped away to provide the air-stable product in quantitative yield.

30

Example 2

Preparation Of $(C_6F_5)_3B \cdot H_2O$

A mixture of 0.566 gram (1 mmol) $(C_6F_5)_3B \cdot 3H_2O$ as prepared in Example 1 and 1.024 grams (2 mmol) $(C_6F_5)_3B$ in 10 mL dichloromethane was stirred for 15 minutes and then evaporated to dryness under vacuum. A quantitative yield of the product remained and was

stored under dry nitrogen.

Example 3

Preparation of $[\text{Et}_3\text{NH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$

5 A solution of 3.6 grams $(\text{C}_6\text{F}_5)_3\text{B} \cdot 3\text{H}_2\text{O}$ as prepared in Example 1 in 20 mL toluene was treated with 0.76 gram triethylamine in 3 mL of the same solvent. The reaction mixture was diluted with 50 mL hexane to precipitate 2.75 gram of crude product. Using Karl
10 Fisher analysis, the crude product was determined to be a hydrate and the % H_2O present was 0.66. The crude product was recrystallized by solution in a minimum amount of hot toluene, followed by cooling to -50°C . Filtration and vacuum drying yielded a material
15 containing 0.15 % H_2O (by weight), corresponding to 5 mole per cent H_2O .

Example 4

Preparation of $(\text{C}_6\text{F}_5)_3\text{B} \cdot 2\text{MeOH}$

A solution of 0.34 gram of $(\text{C}_6\text{F}_5)_3\text{B}$ in 1.5 mL
20 methanol was prepared under dry N_2 and evaporated to dryness to yield a clear viscous residue that crystallized under dynamic vacuum (vacuum pumping) overnight. The yield was 0.33 gram.

Example 5

Preparation of $[\text{Ph}_3\text{PMe}][(\text{C}_6\text{F}_5)_3\text{BOMe}]$

A solution of 0.39 gram (0.76 mmol) of $(\text{C}_6\text{F}_5)_3\text{B}$ in 1
mL methanol was treated with a slight excess (>5%) of
methanolic sodium methoxide. Excess
30 methyltriphenylphosphonium bromide was then added to the solution. The solution was diluted to the cloud point with water and then refrigerated. White crystals were collected on a filter, washed with water and vacuum dried. The yield was 0.58 grams (93%).

Example 6

A similar reaction to Example 5 was used to prepare the triethylammonium salt but, under these conditions, partial hydrolysis of the anion to
5 $(C_6F_5)_3BOH^-$ occurred.

Example 7**Preparation of $(C_6F_5)_3B \cdot C_{18}H_{37}OH$**

A solution of 0.135 gram (0.5 mmol) of 1-octadecanol and 0.256 gram (0.5 mmol) of $(C_6F_5)_3B$ in 4
10 mL toluene was stirred for 30 minutes. The solution was then evaporated on a vacuum line. The remaining product was as a viscous oil, and the yield was approximately 0.37 gram. The $(C_6F_5)_3B$ complex was prepared and handled in an atmosphere of dry nitrogen.

15

Example 8**Preparation of $(C_6F_5)_3B \cdot C_{18}H_{37}SH$**

A solution of 0.143 gram (0.5 mmol) of 1-octadecyl mercaptan and 0.356 gram (0.5 mmol) of $(C_6F_5)_3B$ in 5 mL
20 dichloromethane was evaporated under high vacuum. The residual product was an oil weighing 0.36 gram.

Example 9**Preparation of $(C_6F_5)_3B \cdot C_4H_9OC_2H_4OH$**

A solution of 0.059 gram (0.5 mmol) of 2-butoxyethanol, dried over 4A molecular sieves and 0.256 gram (0.5 mmol) of $(C_6F_5)_3B$ in 1 mL toluene was evaporated under high vacuum. The residual product was a viscous oil and the yield was approximately 0.24
30 gram.

Example 10**Preparation of $(C_6F_5)_3B \cdot \text{cyclo-}C_6H_{10}=NOH$**

A solution of 0.056 gram (0.5 mmol) of cyclohexanone oxime and 0.256 gram of $(C_6F_5)_3B$ in 2.5 mL
35 dichloromethane was evaporated under high vacuum to leave 0.28 gram of product.

Example 11**Preparation of $(C_6F_5)_3B \cdot (Me_3SiO)_3SiOH$**

A solution of 0.312 gram (1 mmol) of tris(trimethylsiloxy)silanol (PCR, Inc., Gainesville, FL) and 0.512 gram (1 mmol) of $(C_6F_5)_3B$ in 1.5 mL toluene was stirred for 30 minutes and then evaporated under high vacuum. There remaining 0.8 gram of product was a white semi-solid.

Example 12**Fluorinated alcohol complex**

Tris(pentafluorophenyl)borane (0.51 gram, 1 mmol) and 0.44 gram (1 mmol) of $CF_3CF_2(CF_2CF_2)_nCH_2CH_2OH$ (as prepared in U.S. Patent No. 4,219,681, Example 1 and such description is incorporated herein by reference) in which the average value of n was 3.5 were combined under dry nitrogen in 2 mL of $CF_2ClCFCl_2$. After stirring the solution for approximately 1 hour, the solvent was evaporated to leave a fluorinated alcohol complex as a greasy solid.

Example 13**Polymerization using $(C_6F_5)_3B \cdot H_2O$** **1. Preparation of $(C_5H_5)_2ZrMe_2$**

$(C_5H_5)_2ZrMe_2$ was prepared by treatment of $(C_5H_5)_2ZrCl_2$ in diethyl ether with two equivalents of methyl lithium as described in Samuel et al. *J. Am. Chem. Soc.* 1973, 9, 6263.

2. 1-Hexene (0.67 gram) was added under nitrogen to a catalyst prepared by combining 0.05 mmole each of $(C_6F_5)_3B \cdot H_2O$ prepared according to Example 2 and $(C_5H_5)_2ZrMe_2$. After a few seconds, an exothermic reaction occurred and the mixture became thick. After approximately 50 minutes, any suspended catalyst was removed by centrifugation. Unreacted monomer was then evaporated. NMR (1H) analysis showed that the resultant polymer had a number average molecular weight (M_n) of

400. The yield of polymer was 95%.

Example 14

Polymerization using $(\text{Me}_5\text{Cp})\text{HfMe}_3$

- 5 1. Preparation of $(\text{Me}_5\text{Cp})\text{HfMe}_3$
 $(\text{Me}_5\text{Cp})\text{HfMe}_3$ was prepared by reacting $(\text{Me}_5\text{Cp})\text{HfCl}_3$ with 3 equivalents of methyllithium as described in Schock et al. *J. Am. Chem. Soc.* 1988, 110, 7701.
2. A reaction similar to that in the Example 13 was
10 carried out using $(\text{Me}_5\text{Cp})\text{HfMe}_3$ instead of $(\text{C}_5\text{H}_5)_2\text{ZrMe}_2$.
The yield of polymer, with an Mn of 2200, was 90%.

Example 15

Polymerization using $[\text{Et}_3\text{NH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$

- 15 To 0.31 gram (0.5mmol) of $[\text{Et}_3\text{NH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$ (as prepared in Example 3) suspended in 6 mL toluene was added dropwise under dry nitrogen with stirring 0.13 gram (0.5 mmol) $(\text{C}_5\text{H}_5)_2\text{ZrMe}_2$ (as prepared in Example 13(1)) in 1 mL of the same solvent. Gas evolution
20 occurred. The resulting orange oil that separated was removed by decantation, washed with toluene, then hexane, and vacuum dried to give 0.31 gram of catalyst as an orange foam.

- This catalyst (0.01 gram) was added under dry
25 nitrogen to 0.67 gram of 1-hexene. After 3 days, the reaction mixture was diluted with hexane and filtered to remove any undissolved catalyst. Evaporation of the hexane left 0.45 gram of polymer. Gel permeation chromatography (GPC) revealed that the product had $M_w =$
30 27,700, $M_n = 9100$ and $\text{PD} = 3.04$.

Example 16

Soluble catalyst prepared using $(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{C}_{18}\text{H}_{37}\text{OH}$

- 35 A solution of 0.05 mmol $\text{C}_{18}\text{H}_{37}\text{OH}$ in 0.3 mL toluene was added under dry N_2 to 0.05 mmol of $(\text{C}_6\text{F}_5)_3\text{B}$. Then, 0.05 mmol of $(\text{C}_5\text{H}_5)_2\text{HfMe}_2$ as prepared in Example 14 was added to the solution. Approximately, one half of the

resulting catalyst solution was added with stirring to 13.4 gram dry, oxygen-free 1-hexene that had been cooled to 0°C, the monomer:catalyst ratio was 6400:1. The reaction mixture was essentially clear and transparent, that is, no suspended solids were observed. After approximately 16 hours, the polymer product was removed from the reactor by dissolution in hot heptane. After the heptane had been stripped at 95°C using a water aspirator, 13.6 grams of polymer remained having $M_w = 148,000$, $M_n = 55,500$ and $PD = 2.67$.

Examples 17(a) and 17(b)

Reactions similar to Example 16 were carried out using the boron complex prepared according to Example 16 and

(a) $(Me_3SiC_5H_4)_2HfMe_2$ was prepared by reacting $Li[Me_3SiC_5H_4]$ and $HfCl_4$ in tetrahydrofuran followed by alkylation with methyllithium. The monomer:catalyst ratio was 6400:1. The resulting polymer had an M_n of 5040 as determined by NMR analysis; and

(b) $(n-C_8H_{17}C_5H_4)_2HfMe_2$ was prepared by reacting NaC_5H_5 in liquid ammonia with 1- $C_8H_{17}Br$ to provide $n-C_8H_{17}C_5H_5$. This was then converted by reaction with $n-C_4H_9Li$ and then $HfCl_4$ to provide $(n-C_8H_{17}C_5H_4)_2HfCl_2$. Subsequent alkylation with methyllithium produced $(n-C_8H_{17}C_5H_4)_2HfMe_2$. The monomer:catalyst ratio was 3200. The resulting polymer had an M_n of 1932 as determined by NMR analysis.

Example 18

Polymerization using oligomeric (polyhexene) alcohol

A reaction like that in Example 16 was carried out using an oligomeric (polyhexene) alcohol (average degree of polymerization 5.9) instead of octadecanol. The oligomeric (polyhexene) alcohol was prepared according to the procedure described in Examples 1a and 1b of co-pending U.S. patent application, Serial No.

07/_____, filed April 9, 1992 (Attorney Docket No. 47866USA5A) and such description is incorporated herein by reference. The yield of polymer was essentially quantitative. GPC analysis showed the polymer had $M_w =$
5 164,000, $M_n = 63,000$ and PD = 2.6.

Example 19

Comparative example using background art catalyst

Hexene was catalytically polymerized using
10 $[(C_5H_5)_2HfMe][MeB(C_6F_5)_3]$, similar to the Zr analogue described in Yang et al. *J. Am. Chem. Soc.* 1991, 113, 3623.

Cp_2HfMe_2 and $(C_6F_5)_3B$ (0.025 mmol each) were combined in 0.7 mL anhydrous toluene in a dry nitrogen
15 atmosphere. Reaction occurred and a yellow oil separated. The yellow oil was dispersed by shaking and added to 13.4 grams of dry, oxygen-free 1-hexene at 0°C. Separation of a solid catalyst phase was observed. After approximately 48 hours, the resultant
20 polymer was removed from the reactor by dissolving it in hot cyclohexane. The polymer, after removing the solvents under water aspirator vacuum weighed 13.6 grams (some residual solvent was present). GPC analysis revealed that the polymer had $M_w = 48,000$,
25 $M_n = 13,500$ and PD = 3.55. The molecular weight of the polymer was lower, and the polydispersity higher than that of the material produced under similar conditions in Example 16.

Example 20

Polymerization using $(C_6F_5)_3B \cdot C_{18}H_{37}SH$

To a solution of 0.05 mmol of the 1-octadecyl mercaptan complex of $(C_6F_5)_3B$ as prepared in Example 8 was added under nitrogen with stirring 0.024 gram (0.05
35 mmol) of $(Me_3SiCp)_2HfMe_2$ in 0.1 mL anhydrous toluene. This mixture was then added to 13.4 grams of dry, oxygen-free 1-hexane. After approximately 48 hours,

the polymer was dissolved in heptane, and then filtered through a pad of granular alumina. After evaporation of the solvent under reduced pressure, there remained 10.2 grams of polymer having an M_n of 4900 as determined by ^1H NMR.

Example 21

Polymerization using $(\text{C}_6\text{F}_5)_3\text{B} \cdot (\text{MeSiO})_3\text{SiOH}$

A toluene solution (0.3 mL) containing 0.025 mmol each $(\text{C}_6\text{F}_5)_3\text{B} \cdot (\text{Me}_3\text{SiO})_3\text{SiOH}$ and $(\text{indenyl})_2\text{HfMe}_2$ as prepared in Example 14 was added with stirring to 13.4 grams of dry, oxygen-free 1-hexene that had been cooled to 0°C . After approximately 16 hours at this temperature, the polymer weighed 23 grams. NMR analysis disclosed that the polymer contained 5 mole % 4-methyl-1-pentene. According to GPC analysis, the polymer had $M_w = 207,000$, $M_n = 62,000$ and PD 3.3. reactor was opened to air, a small amount of toluene was added and the resulting product scraped into a jar. After the volatiles were removed at $95^\circ\text{C}/6.7$ hPa (5 mm Hg), 11.3 grams of polymer remained. The polymer had an $M_w = 340,000$, $M_n = 145,000$ and PD = 2.34.

Example 22

Polymerization using $(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{cyclo-C}_6\text{H}_{10}=\text{NOH}$

A suspension in 0.85 mL toluene of a catalyst prepared from 0.025 mmole each of the $(\text{C}_6\text{F}_5)_3\text{B} - \text{cyclohexanone oxime}$ complex as prepared in Example 10 and $(\text{indenyl})_2\text{HfMe}_2$ was added with stirring to 13.4 grams of cold (0°C) dry, oxygen-free 1-hexene. After approximately 16 hours, the organic phase was removed and evaporated to give 1.2 grams of polymer having M_n of 31,000 as determined by NMR analysis.

Example 23**Polymerization using $(C_6F_5)_3B \cdot BuOC_2H_4OH$**

In 0.3 mL anhydrous toluene were combined 0.025 mmole each of the butoxyethanol complex as prepared in Example 9 and $(indenyl)_2HfMe_2$. Then 0.67 gram of 1-hexene was added. After approximately 16 hours, the reaction mixture was evaporated to give 0.44 gram (66%) of polymeric product having M_n of 18,000 as determined by NMR.

10

Example 24**Copolymerization of 1-hexene and 4-methyl-1-pentene**

This example illustrates the preparation of a copolymer of two different olefins. A catalyst was prepared from 0.025 mmole each $(indenyl)_2HfMe_2$ and $(C_6F_5)_3B \cdot C_{18}H_{37}OH$ as prepared in Example 7 in 0.3 mL of dry, oxygen-free toluene. The catalyst was added with stirring to a mixture of 26.8 grams of dry, oxygen-free 1-hexene and 2.6 grams of 4methyl-1-pentene that had been cooled to 0°C. After four days, the resulting rigid reaction product was dissolved in 50 mL of toluene and poured into 200 mL of methanol to precipitate the product. After drying in a vacuum oven, the polymer weighed 23 grams. NMR analysis disclosed that the polymer contained 5 mole % 4-methyl-1-pentene. According to GPC analysis, the polymer had $M_w = 207,000$, $M_n = 62,000$ and PD 3.3.

15

20

25

Example 25**Preparation of high molecular weight polyhexene**

A solution of 0.025 mmole $(fluorenyl)_2ZrMe_2$ (as described in Samuel et al. *J. Organomet. Chem.* 1976, 113, 331) in 0.5 mL of anhydrous toluene was added under N_2 to 0.025 mmole $(C_6F_5)_3B \cdot C_{18}H_{37}OH$ as prepared in Example 7 in 0.5 mL toluene. The resulting catalyst was added to 13.4 grams of 1-dry, oxygen-free 1-hexene at 0°C. The mixture was too thick to stir with a

30

35

magnetic stirrer after 10 minutes. After approximately 16 hours, the reactor was opened to air and the contents dissolved in hot toluene. This solution was poured with stirring into a large excess of methanol.

5 After drying in a vacuum oven, the precipitated polymer weighed 9.2 grams. Low angle laser light scattering demonstrated that M_w was 2.15×10^6 . The polydispersity of the polymer was not obtainable because M_n was not independently known. However, polyhexenes were made

10 using the closely related $C_{18}H_{37}OB(C_6F_5)_3$ salts of (cyclopentadienyl) $_2$ HfMe $^+$ and (indenyl) $_2$ HfMe $^+$. The polymer polydispersities were 2.7 and 2.6 respectively. These are entries 8 and 10 shown in Table 1. Since polydispersity is essentially unaffected by

15 introduction of one fused benzene ring onto the cyclopentadienyl ligand it is believed the polyhexene prepared according to this and Example 26, wherein the ligand bound to the metal has two fused benzene rings, has a polydispersity of about three or less.

20

Example 26

High molecular weight polyhexene

A reaction similar to that Example 25 was carried out using less catalyst such that the monomer:catalyst

25 ratio was 37,700:1. Workup was accomplished by scraping the product from the reactor. From 40.2 grams of 1-hexene was obtained 9.8 grams of polymer. Light scattering analysis revealed that M_w was 3,390,000.

30

Example 27

Polymerization of 1-octadecene

A solution in 0.5 mL toluene of the catalyst prepared as in Example 24 was added with stirring to 13.4 grams of 1-octadecene at 0°C. After approximately

35 16 hours, the crude product was slurried with warm isopropanol then dried at 160°C/40 Pa (0.3 mm Hg) to give 13.4 grams (85%) of a waxy polymer (m.p. 45°C).

GPC analysis indicated the polymers had a $M_w = 154,000$, $M_n = 72,000$ and $PD = 2.14$.

Example 28

5 Copolymerization of 1-hexene and 1,13-tetradecadiene

This example illustrates copolymerization of an olefin and a diolefin. A solution containing 0.025 mmole of the catalyst as prepared as Example 24 was added with stirring to a cold (0°C) mixture of 26.8 (319 mmol) of 1-hexene and 0.17 grams (0.88 mmol) of 1,13- $C_{14}H_{26}$, (Shell Co., Houston, TX). After approximately 16 hours at this temperature, the insoluble, tough, rubbery polymer was removed from the reactor, cut into small pieces, and then dried at 80°C under vacuum. The yield was 25.4 grams (94%).

A similar example was run but using instead 0.85 gram of the same diene. The yield of polymer, after vacuum drying, was 25.4 grams (92%).

Example 29

20

Polymerization of ethylene

In a nitrogen-filled drybox, a solution of 0.05 mmole of (indenyl) $_2TiMe_2$ as prepared according in 0.5 mL toluene was added to 0.05 mmole of $C_6F_5B \cdot C_{18}H_{37}OH$ in 0.5 mL of the same solvent. The flask was attached to a vacuum line, the contents frozen and the nitrogen pumped away. After thawing, ethylene was admitted until the pressure reached 80 kPa (600 mm Hg). The reactor was stirred and more ethylene was added so as to maintain the pressure at approximately 80 kPa during the exothermic polymerization. After ethylene consumption had declined, the now-solid reaction mixture was rinsed from the flask with methanol and air dried. The yield of polyethylene, identified by infrared spectroscopy, was 0.65 gram.

Example 30

Preparation of poly(cyclopentene)

This example illustrates the polymerization of a cyclo-olefin. To 14.7 grams of cyclopentene that had been cooled to 0°C was added a solution in 0.4 mL of
5 toluene of the catalyst as prepared in Example 24. The reactor was maintained at this temperature and shaken occasionally. After two days, the mixture was filtered. The solid phase, 1.4 grams, was digested with 50 mL of hot toluene to remove lower molecular
10 weight oligomers and then filtered to provide 0.8 gram of a white, insoluble solid. It was identified by infrared spectroscopy and X-ray powder diffraction as poly(cyclopentene).

Various modifications and alterations of this
15 invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set fourth herein.

CLAIMS:

1. A borane complex comprising:
 - (a) tris(pentafluorophenyl)borane and
 - (b) at least one complexing compound

5 selected from the group comprising water, alcohol, mercaptan, silanols, and oximes.

2. The borane complex according to claim 1, having the general formula:

$$10 \quad (C_6F_5)_3B-(YXH)_q$$

wherein X is oxygen, or sulfur;
 q is 1 to 3;
 Y is a hydrogen atom, R^1- , $(R^2)_3Si-$, or $(R^3)_2C=N-$;

15 R^1 is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a halogen-containing hydrocarbyl group;

R^2 is independently a linear or branched alkyl

20 group containing 1 to 25 carbon atoms, or a phenyl group, further R^2 may contain a $SiO-$ group; and

R^3 is independently a hydrocarbyl group containing 1 to 25 carbon atoms, R^3 may be a hydrogen

25 atom provided both R^3 groups selected are not hydrogen atoms.

3. The borane complex according to claim 1, wherein the R^1 group is $CH_3OC_2H_4-$, t-butylcyclohexyl,

30 isopropyl, allyl, benzyl, methyl, ethyl, $CF_3CF_2(C_2F_4)_nC_2H_4-$, where n has an average value of 3.5, $n-C_{18}H_{37}-$, or poly- α -olefin oligomer containing 2 to 100 olefin monomer units.

4. The borane complex according to claim 1,

35 wherein Y is $(t-C_4H_9)((CH_3)_2Si-$ or $((CH_3)_3SiO)_3Si-$.

5. The borane complex according to claim 1,
wherein the borane complex is $(C_6F_5)_3B \cdot R^1OH$.

6. The borane complex according to claim 1,
5 wherein the borane complex is $(C_6F_5)_3B \cdot R^1SH$.

7. The borane complex according to claim 1,
wherein the borane complex is $(C_6F_5)_3B \cdot (R^2)_3SiOH$.

8. The borane complex according to claim 1,
10 wherein the borane complex is $(C_6F_5)_3B \cdot (R^3)_2C:NOH$.

9. The borane complex according to claim 1,
wherein the borane complex is $(C_6F_5)_3B \cdot 3H_2O$.

15 10. The borane complex according to claim 1,
wherein the borane complex is $(C_6F_5)_3B \cdot H_2O$.

11. A catalyst comprising (a) a borane complex
and (b) a Group IVB organometallic compound.

20

12. The catalyst according to claim 1, wherein
the borane complex is neutral and has the general
formula $(C_6F_5)_3B \cdot (XYH)_q$ and the Group IVB organometallic
compound has the general formula $(Cp)_pM(R^4)_{4-p}$

25 wherein M is titanium, zirconium or hafnium;

X is oxygen, or sulfur;

p is 1 or 2;

q is 1 to 3;

Y is a hydrogen atom, R^1- , $(R^2)_3Si-$, or $(R^3)_2C=N-$;

30

Cp is a cyclopentadienyl ligand, wherein each

carbon atom in the ligand may be,

independently, substituted with a radical

selected from the group consisting of

hydrocarbyl radicals, hydrocarbyl-substituted

35

metalloid radicals wherein the metalloid is

selected from Group IVA of the hydrocarbyl

and substituted-hydrocarbyl radicals contain

1 to 20 carbon atoms and further can include straight and branched alkyl groups, cyclic hydrocarbon groups, alkylsubstituted cyclic hydrocarbon groups, aromatic groups or alkyl-substituted aromatic groups; one or two pairs of adjacent hydrogen atoms of the cyclopentadienyl ligand may be substituted with one or two $-(CH)_4$ groups to form indenyl or fluorenyl radicals, respectively, or compounds in which one or two methylene rings having the general formula $(CH_2)_n$ wherein n is 3 to 6 in the cyclopentadienyl ligand; further, when p is 2 the cyclopentadienyl ligand may be combined into one bidentate ligand molecule by connecting the cyclopentadienyl ligands by an organic or organometalloid group; and

R^1 is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a halogen-containing hydrocarbyl group;

R^2 is independently a linear or branched alkyl group containing 1 to 25 carbon atoms, or a phenyl group, further R^2 may contain a SiO-group; and

R^3 is independently a hydrocarbyl group containing 1 to 25 carbon atoms, R^3 may be a hydrogen atom provided both R^3 groups selected are not hydrogen atoms.

R^4 is independently hydrogen or a hydrocarbyl or substituted hydrocarbyl group containing from 1 to 20 carbon atoms and may be a straight or branched alkyl group, and if sufficiently large enough, a cyclic hydrocarbyl group, an alkyl-substituted cyclohydrocarbyl group, an aromatic group, an aromatic-substituted alkyl group, or an alkylsubstituted aromatic group

and also include trisubstituted organometalloid groups of Group IVA elements wherein each hydrocarbyl group on the metalloid contains from 1 to 20 carbon atoms.

5

13. The catalyst according to claim 12, wherein Cp is a substituted or unsubstituted cyclopentadienyl, indenyl, or fluorenyl group.

10

14. The catalyst according to claim 12, wherein p is 2 and Cp is a cyclopentadienyl group.

15. The catalyst according to claim 12, wherein p is 2 and Cp is a indenyl group.

15

16. The catalyst according to claim 12, wherein p is 1 and Cp is a pentamethyl cyclopentadienyl group.

17. The catalyst according to claim 12, wherein p is 2 and Cp is fluorenyl group.

20

18. The catalyst according to claim 12, wherein XY is an oligomeric O-(poly- α -olefin) group.

19. The catalyst according to claim 12, wherein XY is $\text{OC}_{18}\text{H}_{37}$.

25

20. The catalyst according to claim 12, wherein XY is $\text{SC}_{18}\text{H}_{37}$.

30

21. The catalyst according to claim 11, wherein the borane complex is an acidic salt wherein the anion has the general formula $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{XY}$ and the Group IVB organometallic compound has the general formula

35 $(\text{Cp})_p\text{M}(\text{R}^4)_{4-p}$

wherein M is titanium, zirconium or hafnium.

X is oxygen, or sulfur;

p is 1 or 2;

Y is a hydrogen atom, R^1- , $(R^2)_3Si-$, or $(R^3)_2C=N-$;

Cp is a cyclopentadienyl ligand, wherein each

carbon atom in the ligand may be,

5 independently, substituted with a radical
selected from the group consisting of
hydrocarbyl radicals, hydrocarbyl-substituted
metalloid radicals wherein the metalloid is
10 selected from Group IVA of the periodic table
of the elements, and wherein the hydrocarbyl
and substituted-hydrocarbyl radicals contain
1 to 20 carbon atoms and further can include
straight and branched alkyl groups, cyclic
15 hydrocarbon groups, alkylsubstituted cyclic
hydrocarbon groups, aromatic groups or alkyl-
substituted aromatic groups; one or two pairs
of adjacent hydrogen atoms of the
cyclopentadienyl ligand may be substituted
20 with one or two $-(CH)_4$ groups to form indenyl
or fluorenyl radicals, respectively, or
compounds in which one or two methylene rings
having the general formula $(CH_2)_n$ wherein n is
3 to 6 in the cyclopentadienyl ligand;
25 further, when p is 2 the cyclopentadienyl
ligand may be combined into one bidentate
ligand molecule by connecting the
cyclopentadienyl ligands by an organic or
organometalloid group; and

30 R^1 is a hydrocarbyl group containing 1 to 500
carbon atoms, and may contain a divalent
oxygen and further may be a halogen-
containing hydrocarbyl group;

R^2 is independently a linear or branched alkyl
group containing 1 to 25 carbon atoms, or a
35 phenyl group, further R^2 may contain a SiO-
group; and

R^3 is independently a hydrocarbyl group containing

1 to 25 carbon atoms, R^3 may be a hydrogen atom provided both R^3 groups selected are not hydrogen atoms.

5 R^4 is independently hydrogen or a hydrocarbyl or substituted hydrocarbyl group containing from 1 to 20 carbon atoms and may be a straight or branched alkyl group, and if sufficiently large enough, a cyclic hydrocarbyl group, an alkyl-substituted cyclohydrocarbyl group, an aromatic group, an aromatic-substituted alkyl group, or an alkylsubstituted aromatic group and also include trisubstituted organometalloid groups of Group IVA elements wherein each hydrocarbyl group on the
10 metalloid contains from 1 to 20 carbon atoms.
15

22. A method of polymerizing olefinically unsaturated monomers comprising:

(a) contacting at a temperature range within
20 the range of about -90°C to about 300°C and at a pressure within the range of about 6.9 kPa to 310 MPa (1 to about 45,000 psig) monomers either alone or in combination with one or more monomers in a suitable carrier, solvent or diluent with a catalytically
25 effective amount of the catalyst according to claim 11, or claim 21.

(b) continuing the contacting of step (a) for a sufficient period of time to polymerize at least a portion of said monomers; and

30 (c) recovering a polymer product.

23. The method according to claim 22, wherein the olefinically unsaturated monomers have from 2 to 30 carbon atoms.

24. The method according to claim 23, wherein the olefinically unsaturated monomers have from 5 to 10 carbon atoms.

5 25. The method according to claim 22, wherein the olefinically unsaturated monomers are selected from the group consisting of linear- and branched α -olefins, cyclic olefins, olefins containing an aromatic group, olefins containing silicon and boron, diolefins and
10 mixtures thereof.

26. A polymer prepared according to claim 22, wherein the polymer has a weight average molecular weight of 100,000 to 5,000,000 and a polydispersity
15 (PD) of molecular weights of less than or equal to 3.5.

27. A polymer prepared according to claim 25, wherein the starting olefinically unsaturated monomer is 1-hexene and the polymer has a weight average
20 molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

28. A polymer prepared according to claim 25, wherein the starting olefinically unsaturated monomer
25 is 1-octene and the polymer has a weight average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

29. A polymer of a C_nH_{2n} monomer wherein $n \geq 5$ and
30 having weight average molecular weight of 100,000 to 5,000,000 and a polydispersity (PD) of molecular weights of less than or equal to 3.5.

30. A poly(1-hexene) polymer having a weight
35 average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

31. A poly(1-octene) polymer having a weight average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.